STUDIES OF COAL PYROLYSIS AND COAL
EXTRACTION USING IN-SITU ESR SPECTROSCOPY

Mohindar S. Seehra
Physics Department, West Virginia University
Morgantown, West Virginia 26506

ABSTRACT

Important features of recent results on the pyrolysis and solvent extraction of
American coals (H/C between 0.55 and 0.81) using in-situ ESR spectroscopy are
presented. In the pyrolysis studies, the temperature variation of the free
radical density between 25°C and 650°C establishes the presence of four distinct
stages in about a dozen coals studied. Extraction of the coals with N-Methyl
Pyrrolidone shows an inverse correlation between percentage extraction and room
temperature free radical density. Significance of these results is discussed.

INTRODUCTION

Electron spin resonance (ESR) due to free radicals in coals was discovered in
1954 [1,2]. Since then, some correlations between the ESR parameters of the
free radicals in coals and various properties of coals (such as rank [3],
heteroatom content [4], liquefaction [5] and coking behavior [6]) have been
reported. Recently we developed a heated gas-flow system in which in-situ ESR
spectroscopy of samples could be carried out between room temperature and 650°C.
This apparatus has been used to study pyrolysis behavior of about a dozen
American coals with atomic H/C varying between 0.55 and 0.81. One of the most
significant results of this study is the discovery of four distinct temperature
regions in these coals from the temperature variation of the free radical
density [7-9]. Following this work, Fowler et al [10] have confirmed the
preesence of similar regions in some British coals. Although some explanations
have been advanced for these regions in earlier studies [7-10], additional
discussion on these temperature regions or stages as well as some details of the
high-temperature apparatus used in this work, are presented in this paper. We
also examine the use and limitations of ESR in the studies of the extraction and
de-ashing of coals with N-Methyl pyrrolidone (NMP), a subject of considerable
current interest [11,12].

THE HIGH TEMPERATURE CAVITY SYSTEM

A block diagram of the high-temperature microwave cavity system used for the in-
situ ESR studies for temperatures to 650°C is shown in Fig. 1. All parts with
prefix 'WG' are made of quartz and they were obtained from Wilmad Glass Co. The
system uses a flowing nitrogen gas passing over a heater (powered by a Variac)
to heat the sample located in a TE_{102} mode cavity. To obtain various
temperatures, first the voltage in the Variac is adjusted. Additional control
is provided by adjusting the gas pressure and flow rate. Temperature stability
of ±1°C was obtainable in the whole temperature range studied. Because of the
isolation provided by the quartz dewar, the external temperature of the TE_{102}
cavity, even at 650°C sample temperature, did not exceed 50°C. Since a
thermocouple cannot be placed inside the cavity next to the sample during an ESR
experiment, a separate experiment was carried out to calibrate the thermocouple
placed at the sample position, but without making ESR measurements. Finally, a
screw is used (Fig. 1) to keep the microwave coupling to the cavity constant at
different sample temperatures. Further details of this apparatus are given
elsewhere [13]. Details of the other experimental procedures are given in our
earlier publications [7-9].

RESULTS AND DISCUSSION

A typical variation of the free radical density N_s with temperature for a
representative coal (Matewan coal with $H/C \simeq 0.71$) is shown in Fig. 2. The data
is from Ref. 9 and it shows the four distinct temperature regions mentioned
above in the Introduction. In region 1 ($\sim 25°$-$250°$C) and in region 3 ($\sim 400°$-
$600°$C), the spin concentration N_s increases with increasing temperatures whereas
in region 2 ($250°$-$400°$C) and region 4 ($>600°$C), N_s decreases with increasing
temperatures. Although the locations of these regions or stages differ
slightly from coal to coal on the temperature scale and relative changes in N_s
with temperature are also different for different coals, the qualitative
features of the variation of N_s noted above are the same for all of about dozen
coals studies in our work [7-9]. Recent work of Fowler et al [10] on some
British coals have yielded similar variations for N_s even though their
experiments were done under slightly different conditions viz. flowing N_2 gas
through the samples versue evacuated samples in our case. Note that N_s
represents the spin density corrected for the Curie variation [7-10].

As an aid to interpret the results, we show in Fig. 2b the schematic variation
of the CO_2 internal surface area as a function of the charring temperature for a
bituminous coal (Saline County, Illinois) [14] and in Fig. 2c the temperature
variation of the sample weight for a British coal [10]. Although the results in
Figs. 2a, 2b and 2c are for different coals, sufficient evidence exists [7-
10,14] that qualitatively features of these curves are the same for different
coals. It is evident from Fig. 2 that these different measurements all point to
the distinct temperature stages first highlighted in our ESR work [7]. We now
critically examine the nature of these distinct stages.

The average activation energies, evaluated for stage 1 assuming Arrhenius
variation is $\simeq$ 4 kcal/mol. Since the magnitude is much smaller than that
necessary for bond fission [3,15], stage 1 probably corresponds to the
decomposition of the substituted groups, resulting in the release of CO_2,CO and
H_2O [7,15]. Some decrease in the weight of the samples observed in this region
supports this finding. Fowler et al [10] have noted that increase of N_s in
their samples may partly be due to desorption of oxygen. However this cannot be
the case in our samples because our samples were evacuated and vacuum sealed
prior to experiments.

The decrease in N_s with increasing temperatures in stage 2 is perhaps one of the
more interesting results of these recent studies. Several mechanisms could
contribute to a decrease in N_s:
  a. Recombination of free radicals by thermally activated mobility within
      the pore network;
  b. Previously stable radicals become very reactive, become short-lived and
      hence are not observed;
  c. Quenching of radicals by internally transferred hydrogen; and
  d. Decrease in the surface area leading to the blocking of the pore
      network and recombination.

It is noted that there is no significant loss in the sample weight in this
region so that some kind of quenching or recombination of the radicals is most
likely the cause for the decrease of N_s. We tend to disfavor explanation b
since if this was the mechanism, a broadening of the ESR lines should be
observed. This certainly is not the case [9]. Explanations a and d are related
and they receive strong support from the observed decrease in the surface area

(Fig. 2b and Ref. 14).   It is noted that stage 2 is observed even in treated samples [10] and in residues and extracts after treatment with NMP [12] although the location of the peaks and valleys are affected by the treatment.   Swelling of coals which is observed in many coals in this temperature range is partially due to release of gases such as H_2 and may cause the observed decrease in the internal surface area. H_2 gas is known to quench the free radicals [16].   Thus it is very likely that explanations a, c, and d are simultaneously operative in stage 2, perhaps at different levels in different coals.

In stage 3, the sharp decrease in the sample weight accompanied by the sharp increase in N_s has been interpreted to be due to breaking and rearrangement of the aromatic rings of the coal structure.   The activation energies determined from the temperature dependence of N_s are in the range of 15 kcal/mol [9]. These energies are sufficient for bond fission [3,15].   The fact that the volatiles in this stage contain free radicals further supports this interpretation [17].   In stage 4, the decrease in N_s is most likely to be recombination of free radicals and formation of chars.

The use of ESR spectroscopy in coals treated with solvents such as NMP [12] has led to considerable understanding of the mechanism of coal extraction with these solvents.   There is strong evidence that treatment with NMP extracts exinites and to a lesser degree vitrinites present in coal samples whereas the inertinites and ash are left in the residue [12].   This conclusion is partly based on the observation of the inverse correlation between N_s and percent extraction as exinites have lower free radical density [12].

CONCLUDING REMARKS

In this paper we have discussed some of the recent results obtained with in-situ ESR spectroscopy on coal pyrolysis and coal extraction.   Although many interesting results have been obtained and we have now the capability of measuring ESR due to free radicals at high temperatures at time intervals of one minute or so, the short-lived free radicals are not observed by the steady-state ESR spectroscopy.   The next advance in this area is likely to come from an understanding of the role of short-lived free radicals in coal conversion processes.

ACKNOWLEDGEMENTS

REFERENCES

1. D.J.E. Ingram, J.G. Tapley, R. Jackman, R.L. Bond, and A.R. Murnagham, Nature (London) 174, 797 (1954).

2. J.J. Uebersfeld, J. Phys. Radium 15, 126 (1954).

3. H.L. Retcofsky, J.M. Stark and R.A. Friedel, Anal. Chem. 40, 1699 (1968).

4. H.L. Retcofsky, M.R. Hough, M.M. Maguire and R.B. Clarkson in 'Coal Structure', (Eds. M.L. Gorbaty and K. Ouchi) Am. Chem. Soc. Advances in Chem. Series, 192, 1981.

5. L. Petrakis and D.W. Grandy, 'Free Radicals in Coals and Synthetic Fuels' (Elsevier, 1983).

6. M. Sakawa, T. Uno, and Y. Hara, Fuel 62, 585 (1983).

7. M.S. Seehra, B. Ghosh, and S.E. Mullins, Fuel 65, 1315 (1986).

8. B. Ghosh and M.S. Seehra, 'Proc. Third Annual Pittsburgh Coal Conf. 1986 (Pittsburgh Coal Conf. MEMS, One Northgate Square, Greensburg, PA 15601) pp. 704-716.

9. M.S. Seehra and B. Ghosh, J. Anal. Appl. Pyrolysis 13, 209 (1988).

10. T.G. Fowler, K.D. Bartle, and R. Kandiyoti, Fuel 66, 1407 (1987).

11. K. Renganathan, J.W. Zondlo, E.A. Mintz, P. Kneisl, and A.H. Stiller, Fuel Process. Tech. (in press).

12. M.S. Seehra, B. Ghosh, J.W. Zondlo, and E. Mintz, Fuel Process. Tech. (in press).

13. S.E. Mullins, M.S. Thesis, West Virginia University, 1987 entitled 'A High Temperature Electron Spin Resonance Cavity System and Coal Pyrolysis Studies'.

14. C.W. Kruse and N.F. Shimp, Coal Processing Tech. 7, 124 (1981).

15. G.R. Gavalas, 'Coal Pyrolysis', Elsevier 1982.

16. G. Srinivasan and M.S. Seehra, Fuel 61, 1249 (1982); ibid 62, 792 (1983).

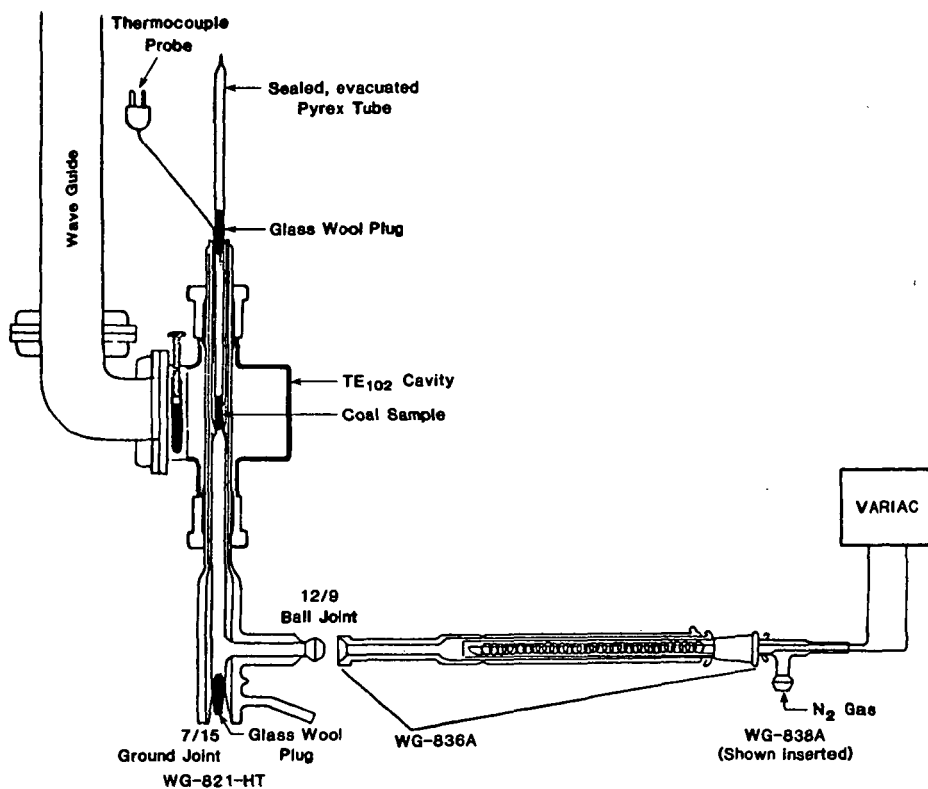17. C.J. Chu, R.H. Hauge, and J.L. Margrave, Am. Chem. Soc. Div. Fuel Chem. Prepr. p. 87 (1986).

Fig. 1. A block diagram of the high-temperature microwave
         cavity system for in-situ ESR studies to 650°C with
         ±1°C stability. Components labelled with prefix
         'WG' are made of quartz and they were obtained from
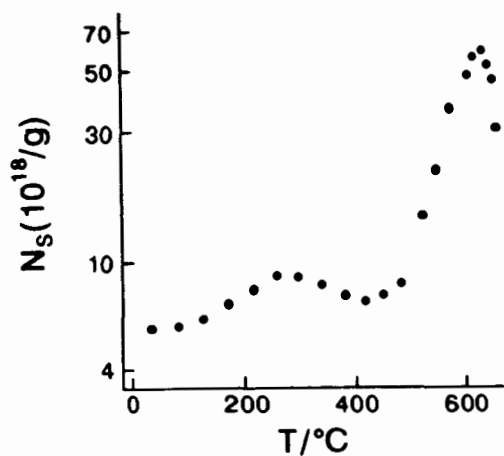   Wilmad Glass Co. (see text for details).

Fig. 2a. Free radical density N_S vs temperature for Matewan coal (Based on Ref. 9).
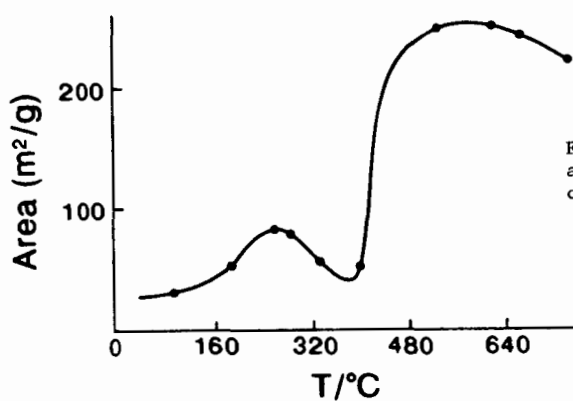

Fig. 2b. Internal CO_2 surface area vs temperature for a coal (Based on Ref. 14).
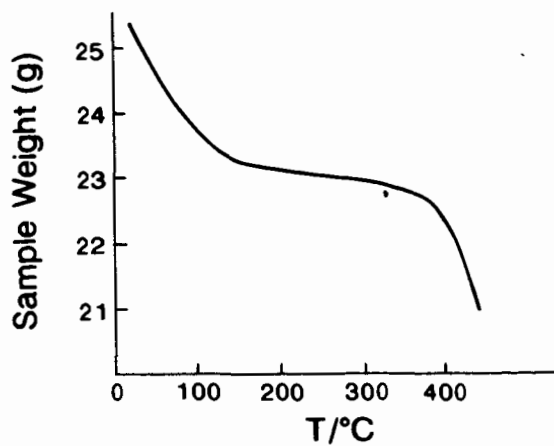

Fig. 2c. Sample weight vs temperature for a British coal (Based on Ref. 10).